Studies on Extraction and Determination of Metal Salts with Methyl Isobutyl Ketone. VI : Photometric Determination of Microquantity of Cobalt and Iron in Metallic Nickel

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Photometric Determination of Microquantity of Cobalt and Iron in Metallic Nickel*

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Synopsis

Studies were made on the determination of microamounts of cobalt and iron in metallic nickel. After extracting the thiocyanate complexes of cobalt and iron in the presence of nickel, simultaneous determination of cobalt and iron was made photometrically and satisfactory results were obtained. However, the above-mentioned simple method was not suitable for the determination of a trace amount of cobalt, and so an improved method was devised to determine about 0.001 per cent of cobalt contained in metallic nickel.

I. Introduction

Determination of cobalt in metallic nickel is usually made by the gravimetric method using 1–nitroso–2–naphthol and also by the nitroso-R salt method as in the case of iron and steel.(1) A method using 2–nitroso–1—naphthol has also been reported.(2) Gravimetric method takes a long time for the analysis and is not suitable for micro-determination. The nitroso-R salt method is usually carried out in the presence of nickel without separation of cobalt, and so that it is simple, but not suitable for microquantity of cobalt. An attempt was, therefore, made to determine microquantity of cobalt in nickel by extracting cobalt as its thiocyanate in the presence of nickel with methyl isobutyl ketone, and to determine both cobalt and iron at the same time. A satisfactory result was thereby obtained. Further, a method suitable for determination of microquantity of cobalt was devised by extending this process.

II. Determination of cobalt and iron

1. Reagents and apparatus

(i) Reagents

Standard cobalt solution: Pure metallic cobalt was weighed accurately,

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* The 1068th report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in Journal of the Japan institute of Metals, **25**, (1961), 181.

(1) A.S.T.M., *Method for Chemical Analysis of Metals* (1956), 225, 244.

(2) A. Classen and A. Daaman, Anal. Chim. Acta, **12** (1955), 543.

dissolved in a small amount of nitric acid, and diluted with water to make a solution contain 1 mg/ml of cobalt. This stock solution was diluted with water when it was used.

Standard iron solution: Electrolytic iron was weighed accurately, dissolved in nitric acid, and diluted with water to make a solution contain 0.1 mg/ml of iron. This stock solution was diluted with water when used.

Ammonium thiocyanate solution: 8 mol/l aqueous solution.

Hydrochloric acid: 10 N solution,

Nitric acid, hydrochloric acid, stannous chloride, and methyl isobutyl ketone: First grade for chemical use.

(ii) Apparatus

Hitachi photoelectric spectrophotometer, model EPU-2, 1-cm cell.

2. Conditions for determination of cobalt

The conditions for determining microquantity of cobalt[3] by extracting its thiocyanate with methyl isobutyl ketone[4] has already been examined. In the present series of work, the determination was made by measuring the absorbance of cobalt complex salt at its absorption maximum of 630 mμ with 0.5N of hydrochloric acid and 4 mol/l of ammonium thiocyanate concentration.

3. Relationship between the amount of cobalt and the absorbance

With various amounts of cobalt and the concentration at 0.5 N of hydrochloric acid and 4 mol/l of ammonium thiocyanate when the whole volume was brought to 10 ml, the extraction was made with 10 ml of methyl isobutyl ketone. The relationship between the amount of cobalt and the absorbance was linear, as shown in Fig. 1.

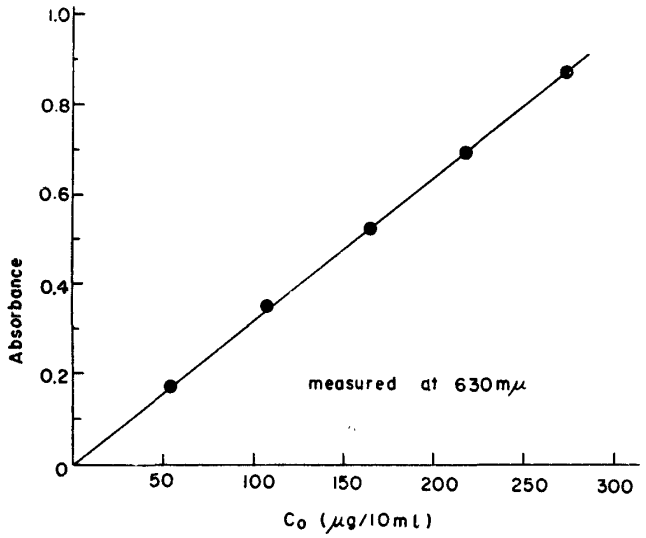

Fig. 1. Relation between amount of Co and absorbance

(3) H. Gotô, Y. Kakita and M. Namiki, J. Japan Inst. Met., **25** (1961), 178; Sci. Rep. RITU, **A 14** (1962), 300.

(4) H. Gotô, Y. Kakita and M. Namiki, J. Chem. Soc. Japan, **82** (1961), 68; Sci. Rep. RITU, **A 14** (1962), 239.

4. Conditions for determination of iron and absorbance curve

In order to determine the microquantity of iron present in the nickel metal at the time that the determination of coablt is made, the conditions for the determination of iron were examined. Iron forms its thiocyanate in the form of iron (III) red in color. This salt was extracted with organic solvents, which was used for the photometric determination of iron[5,6]. The extraction rate of ferric thiocyanate was better with lower concentration of hydrochloric acid and higher concentration of ammonium thiocyanate.[6] The extraction of cobalt at 5N of hydrochloric acid and 4 mol/l of ammonium thiocyanate always give over 99 per cent extraction of iron, and these conditions were adopted to obtain the absorbance curve. With 10.2 μg of iron (III), the concentration of hydrochloric acid, was 0.5N, and ammonium thiocyanate 4 mol/l, when the whole volume was brought to 10ml, the extraction was done with 10ml of methyl isobutyl ketone, and the absorbance of the extract solution was measured at 280~700 mμ. The results shown in Fig. 2 indicate that the absorption maximum lies around 510mμ and only a slight absorption at the absorption maximum of cobalt at 630 mμ. The molecular extinction coefficient at 510mμ is 19500. Although the absorption maximum of iron is at 510 mμ, there is a slight absorption of cobalt, and therefore, iron absorption at 520 mμ where there is no absorption of cobalt, was used for the measurement.

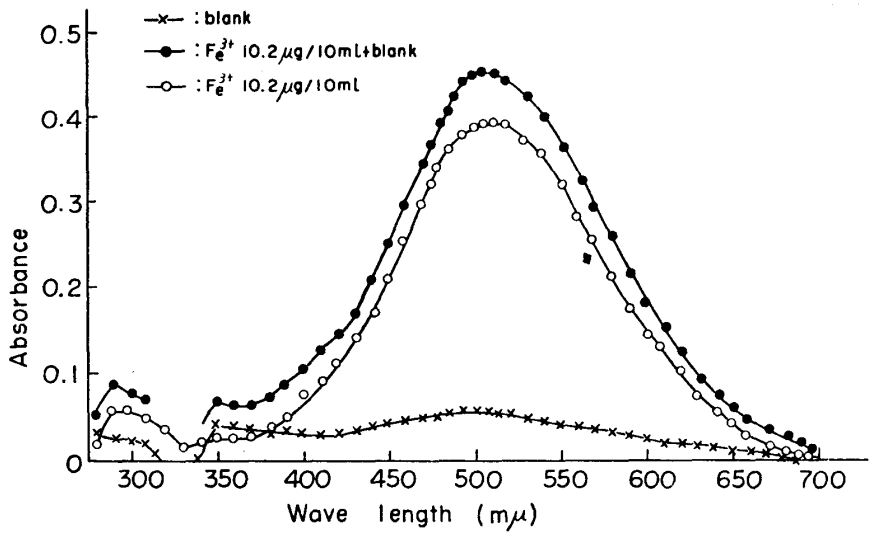

Fig. 2 Absorbance curve

5. Stability of iron (III) complex salt in methyl isobutyl ketone solution

The thiocyanate of iron (III) is unstable in acidic aqueous solution and the color fades easily. Experiments were, therefore, carried out to see its stability in the methyl isobutyl ketone extract. The same procedure as the above was carried

(5) A.S.T.M., *Method for Chemical Analysis of Metals* (1956), 243.
(6) K.W. Kirly and R.H.A. Grawlay, Anal. Chim. Acta, **19** (1958), 363.

Table 1. Effect of standing time.

Standing time	Absorbance		
	Blank	Fe 10μg (against blank)	Fe 20μg (against blank)
At once	0.066	0.360	0.725
15 min	0.070	0.363	0.730
30 min	0.070	0.360	0.730
45 min	0.072	0.362	0.730
1 hr	0.070	0.360	0.720
2 hr	0.070	0.352	0.710
3 hr	0.071	0.349	0.690
4 hr	0.068	0.342	0.685
5 hr	0.067	0.342	0.680
6 hr	0.070	0.348	0.685

out with 10 or 20 μg of iron (III) and the absorbance of the extract solution was measured at 520 mμ, results of which are shown in Table 1. It is seen that the iron (III) complex salt was quite stable in methyl isobutyl ketone solution.

6. Relationship between the amount of iron and the absorbance

The same procedures as the above were carried out with various amounts of iron, and the absorbances of the extract solution were measured at 520 mμ and at 630 mμ for determination of iron and cobalt respectively, to find the relationship between the amount of iron and the absorbance. As shown in Fig. 3 results were linear both at 520 and 630 mμ.

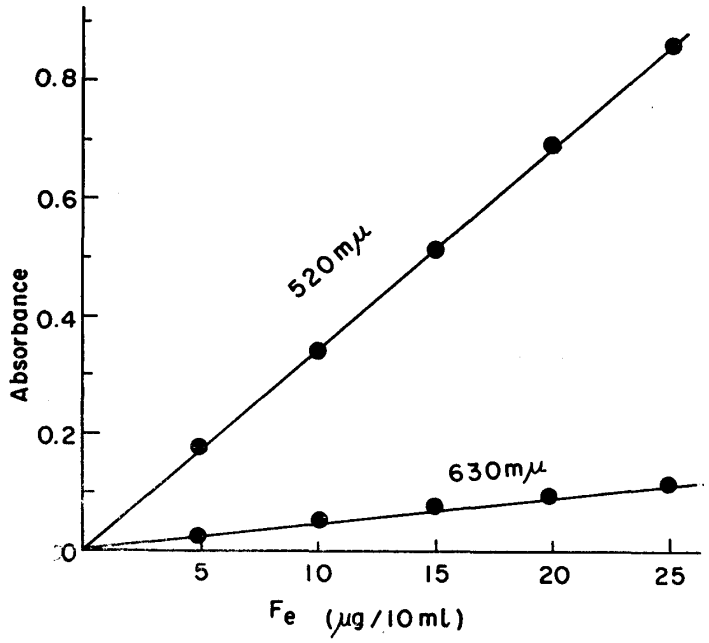

Fig. 3. Relation between amount of Fe and absorbance

III. Determination of cobalt and iron in nickel

An attempt was made to determine simultaneously the microquantity of iron

and cobalt contained in nickel by the present method. The method was so devised that cobalt alone could be determined when the quantity of iron was comparatively large and a simultaneous determination seemed impractical or when determination of iron was not required.

1. Analytical procedure

(i) Simultaneous determination of cobalt and iron (cobalt over 0.01 per cent)

A solution of 0.1 g of the sample dissolved with heating in 10 ml of nitric acid (1: 1) was evaporated to dryness and the residue was dissolved in 5 ml of 10 N hydrochloric acid. The solution was transferred to a separatory funnel with 4.5 ml of water, to which 5 ml of 8 mol/l ammonium thiocyanate was added, and the extraction was carried out with 10 ml of methyl isobutyl ketone. The absorbance of the extract was measured at 630 and 520 mμ.

The absorbance of iron can be measured at 520mμ without any effect of cobalt, and the amount of iron is calculated from the calibration curve at 520mμ. The absorbance of iron at 630mμ is obtained from the calibration curve of iron at 630mμ and this absorbance is subtracted from the absorbance at 630mμ to obtain the absorbance of cobalt. The amount of cobalt is obtained from the calibration curve for cobalt (without adding stannous chloride).

(ii) Determination of cobalt alone

(a) Cobalt content above 0.01 per cent

A solution of 0.1 g of the sample dissolved with heating in 10ml of nitric acid (1: 1) was evaporated to dryness, the residue was dissolved in 0.5 ml of 10N hydrochloric acid, and the solution was transferred to a separatory funnel with the aid of 4.5 ml of water. To this solution 5 ml of 8 mol/l ammonium thiocyanate and 2g of stannous chloride were added, the mixture was shaken to effect solution, and extracted with 5 ml of methyl isobutyl ketone. The absorbance of the extract was measured at 630 mμ and the amount of cobalt was obtained from the calibration curve (with addition of stannons chloride).

(b) Cobalt content of 0.001 per cent to 0.01 per cent

A solution of 0.3~1.0 g of the sample dissolved in 10~20ml of nitric acid (1: 1) was transferred to a separatory funnel with the aid of 12ml of water, and the whole volume was brought to 30ml with addition of 15 ml of 8 mol/l ammonium thiocyanate. This was extracted with 30ml of methyl isobutyl ketone, the aqueous layer was discarded, and the ketone layer was transferred to a beaker. The separatory funnel was washed out with 1.5 ml of methyl isobutyl ketone and the washings were added to the ketone layer. The ketone solution was evaporated, a small amount of nitric and perchloric acid was added, and the mixture was heated to decompose organic matter and evaporated to dryness.

The residue was dissolved in 0.5ml of 10N hydrochloric acid, transferred to a separatory funnel with the aid of 4.5ml of water, and 5ml of 8 mol/l ammonium thiocyanate and 2 g of stannous chloride were added. This mixture was extracted

with 5 ml of methyl isobutyl ketone and the absorbance of the extract was measured at 630 mμ to obtain the amount of cobalt as in the case of (a). With samples containing a comparatively large amount of iron, the solution was evaporated after the first extraction to effect decomposition, the residue was dissolved in a small amount of 8N hydrochloric acid, and iron was extracted with the same volume of methyl isobutyl ketone to remove iron before the next extraction.

(iii) Calibration curve

(a) Calibration curve for iron

Standard iron solution was taken in various amount of 0–25 μg, with 0.5 N of hydrochloric acid and 4 mol/l of ammonium thiocyanate when the whole was brought to 10 ml, and the mixture was shaken vigorously with 10 ml of methyl isobutyl ketone for about 30 seconds. The absorbance of the extract was measured at 520 and 630mμ, and the relationship between the amount of iron and the absorbance at each wave length was plotted.

(b) Calibration curve for cobalt (without addition of stannous chloride)

Standard cobalt solution is taken in various amounts of 0$\sim$250μg and the extraction was carried out as in the case of iron described above. The absorbance of the extract was measured at 630 mμ and the relationship between the amount of cobalt and the absorbance was plotted.

(c) Calibration curve for cobalt (with addition of stannous chloride)

Standard cobalt solution was taken in various amounts of 0$\sim$250μg, extracted with 5 ml of methyl isobutyl ketone under the same conditions as above, but with addition of stannous chloride, and the absorbance of the extract was measured at 630 mμ. The relationship between the amount of cobalt and the absorbance was plotted.

2. Analytical result

Determination of cobalt and iron in prepared samples and in electrolytic nickel was carried out by the present method. Simultaneous determination of cobalt and iron in nickel was first carried out with prepared samples, and the result is given in Table 2. Although there was some slight errors, the determination could be made very easily. Cobalt and iron originally present in the nickel used

Table 2. Simultaneous determination of Co and Fe in synthetic samples.

Ni taken (g)	Fe added (μg)	Co added (μg)	Absorbance		Fe found (μg)	Co found (μg)
			520 mμ	630 mμ		
0.100	5	165	0.180 0.172	0.535 0.560	5.1 4.9	163 170
0.100	10	110	0.351 0.347	0.395 0.387	10.0 9.9	112 102
0.100	15	55	0.523 0.525	0.244 0.233	15.0 15.1	56.2 52.5

Table 3. Simultaneous determination of Co and Fe in nickel sample.

Sample	Sample taken (g)	Absorbance 520mμ	Absorbance 630mμ	Fe found (μg)	Fe (%)	Co found μg)	Co (%)	Co nitroso-R salt method (%)
Electrolytic nickel	0.1000	0.238 0.229	0.300 0.300	6.8 6.5	0.0068 0.0065	86 86	0.086 0.086	—
Nickel A	0.1000 (1/10aliquot)	0.075 0.083	0.232 0.227	21.5 23.0	0.022 0.023	700 690	0.70 0.69	0.71
Nickel B	0.1000 (〃)	0.294 0.306	0.478 0.480	41.8 43.5	0.042 0.044	700 700	0.70 0.70	0.70
Nickel C	0.1000 (〃)	0.366 0.344	0.468 0.470	52.3 48.0	0.052 0.048	665 675	0.67 0.68	0.66

Table 4. Determination of Co in nickel sample.

Sample	Sample taken (g)	Absorbance	Co found (μg)	Co (%)	Co nitroso-R salt mthod (%)
Electrolytic nickel (1)	0.0200 0.0200	0.270 0.275	59.5 60.5	0.300 0.303	0.25
Electrolytic nickel (2)	0.0500 0.0500	0.222 0.220	24.0 22.0	0.048 0.044	0.035
Electrolytic nickel (3)	1.0000 1.0000	0.114 0.115	25.8 26.0	0.0026 0.0026	—
Monde nickel	0.9382 0.9033	0.190 0.169	42.0 38.0	0.0045 0.9042	—

were preliminarily removed by the same method.

The use of this method with actual samples gave the result shown in Table 3 and the determination of cobalt together with that of iron gave the result shown in Table 4.

These results indicate that around 0.001 per cent of cobalt can easily be determined by selecting suitable procedures according to the content of cobalt. In the simultaneous determination of cobalt and iron, the measurement of the absorbance becomes difficult when a large quantity of iron is present, since the molecular extinction coefficient of iron is much larger than that of cobalt. In such a case, cobalt alone should be determined and iron determined with another smaller portion of the same sample.